

# Finite Size Atom in the Hartree-Fock Approximation: New Substance Quasiparticle

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It is shown that, in the self-consistent quantum statistical Hartree-Fock approximation, the number of electronic states localized on one nucleus is finite. This result is obtained on the basis of the general electron-nuclear model of matter and provides convergence of the atomic statistical sum and finiteness of the "atom" size. In general approach the characteristic size of the "atom" is a function of density and temperature. However, it is shown, that in a wide range of thermodynamic parameters, for relatively low temperatures, characteristic orbits and electron energy eigenvalues are independent of density and temperature. In this case, the sizes of the orbits are of order of the Bohr radius which is a minimal characteristic size in the system for typical parameters of plasma with atomic states.

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## I. INTRODUCTION

Real matter (gases, liquids, solids, plasma) is constructed from nuclei and electrons interacting with each other according to the Coulomb law [1]. It would be very desirable, based on the known nucleus charge as an initial problem parameter and, based only on the Coulomb law, to construct a scheme for calculating macroscopic properties of different media. The consistent approach to implement such a scheme is based on the methods of the diagram technique of the perturbation theory [1,2]. The main difficulties in the realization of this approach are caused by the necessity of the simultaneous consideration of both "localized" states of electrons and nuclei ("atoms", "molecules", etc.), whose description requires accurate summation of rows of the perturbation theory, and "delocalized" states which are

quite successfully described within the lowest orders of the perturbation theory [1,2]. As a result, "localized" states for weakly nonideal plasma are considered within the second virial coefficient [1-4]. In this case, there arises the known problem of the convergence of the statistical sum of the hydrogen atom, which is directly related to its size [2]. A large number of works are devoted to the solution of this problem, where various procedures and physical mechanisms of "cutoff" of the statistical sum of the atom were proposed, including the papers [5-12] which have already become classical (see [1-3] and references therein for more details). In this case, the following circumstance is very surprising. As is known [13,14], the self-consistent Hartree-Fock approximation and its various generalizations are basic in calculations of the structure and energy spectra of atoms and molecules in quantum chemistry. Despite the known statement that the self-consistent Hartree-Fock approximation is the best single-particle approximation in quantum statistics [15], it is almost not used in the study of thermodynamic properties of Coulomb systems, where "localized" states should be taken into account [1]. This paper is devoted to the solution of the problem of convergence of the statistical sum of the hydrogen atom and its size finiteness, based on the self-consistent quantum-statistical Hartree-Fock approximation for the Coulomb system.

## II. TWO-COMPONENT ELECTRON-NUCLEAR PLASMA: ADIABATIC APPROXIMATION AND CLASSIFICATION OF THE ELECTRON STATES

We consider the two-component Coulomb system (CS) in volume  $V$  at temperature  $T$  within the canonical ensemble consisting of electrons (subscript  $e$ ) and nuclei (subscript  $c$ ), taking into account the quasineutrality condition  $\sum_{a=e,c} z_a e n_a^{(0)} = 0$ . Here  $n_a^{(0)} = \langle N_a \rangle^{(can)} / V$  is the average density of the number of particles;  $N_a$  is the operator of the total number of particles of type  $a$ , characterized by mass  $m_a$ , the average density of the number of particles  $n_a$ , and charge  $z_a e$ ; angle brackets  $\langle \dots \rangle^{(can)}$  mean averaging over the canonical ensemble. For such a CS, the Hamiltonian  $H^{CS} = H_{ee} + H_{cc} + H_{ec}$  in the secondary quantization representation is written as [1]

$$H_{aa} = -\frac{\hbar^2}{2m_a} \int \psi_a^+(\mathbf{r}) \nabla^2 \psi_a(\mathbf{r}) d\mathbf{r} + V_{aa}, \quad H_{ec} = \int u_{ec}(\mathbf{r}_1 - \mathbf{r}_2) N_e(\mathbf{r}_1) N_c(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (1)$$

$$V_{aa} = \frac{1}{2} \int u_{aa}(\mathbf{r}_1 - \mathbf{r}_2) \psi_a^+(\mathbf{r}_1) \psi_a^+(\mathbf{r}_2) \psi_a(\mathbf{r}_2) \psi_a(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2, \quad u_{aa}(r) = \frac{z_a z_b e^2}{r}, \quad (2)$$

Here  $u_{aa}(r)$  is the potential of the Coulomb interaction of particles of types  $a$  and  $b$ ,  $\psi_a^+(\mathbf{r})$  and  $\psi_a(\mathbf{r})$  are the field creation and annihilation operators,  $N_a(\mathbf{r}) = \psi_a^+(\mathbf{r})\psi_a(\mathbf{r})$  is the density operator of the number of particles of type  $a$ , which, in the coordinate representation, is written as  $N_a(\mathbf{r}) = \sum_{i=1}^{N_a} \delta(\mathbf{r} - \mathbf{R}_i^a)$ . The values  $\mathbf{R}_i^a$  are the coordinates of particles of type  $a$ . We emphasize that the total number of particles  $N_a$  of each type in the canonical ensemble is specified and is the C-number,  $N_a = \int N_a(\mathbf{r})d\mathbf{r} = \langle N_a \rangle^{(can)}$ . The free energy  $F^{CS}$  of the considered quasi-neutral CS consisting of the set number of electrons  $N_e$  and nuclei  $N_c$  in volume  $V$  at temperature  $T$ ,  $F^{CS} = -T \ln Sp \left\{ \exp \left( -\frac{H^{CS}}{T} \right) \right\}$ , in the adiabatic approximation for nuclei, is written as

$$F^{CS} \cong -T \ln Sp_c \left\{ \exp \left( \frac{F_{ec} - H_{cc}}{T} \right) \right\}, \quad F_{ec} = -T \ln Sp_e \left\{ \exp \left( -\frac{H_{ee} + H_{ec}}{T} \right) \right\}. \quad (3)$$

The quantity  $F_{ec}$  (3) is the free energy of the subsystem of electrons being in the external field of stationary nuclei. In this case, the operator of the density of the number of nuclei  $n_c(\mathbf{r})$  in the Hamiltonian  $H_{ec}$  (1) is the C-number. At this stage, when considering the subsystem of electrons in the external field of stationary nuclei, we proceed from the equivalence of the large canonical and canonical ensembles, i.e., we suppose that the equality [16]

$$F_{ec} = \Omega_{ec} + \mu_e \langle N_e \rangle^{(GE)}, \quad \Omega_{ec} = -T \ln Sp_e \left\{ \exp \left[ -\frac{H_{ee} + H_{ec} - \mu_e N_e}{T} \right] \right\}, \quad (4)$$

for the free energy  $F_{ec}$  (3) is valid. In (4) the function  $\Omega_{ec}$  is the thermodynamic potential of the subsystem of electrons with the chemical potential  $\mu_e$  in the external field of stationary nuclei, whose value depends on the nucleus coordinates  $\{\mathbf{R}_i^c\}$  as the external parameters,  $\langle N_e \rangle^{(GE)}$  is the average number of electrons as a function of temperature  $T$ , volume  $V$ , and chemical potential  $\mu_e$ . In this case, the quasineutrality condition takes the form  $\langle N_e \rangle^{(GE)} = z_c N_c$  and is used to determine the chemical potential  $\mu_e$  of electrons.

Then, to describe the field operators  $\psi_a^+(\mathbf{r})$  and  $\psi_a(\mathbf{r})$  in the representation of occupation numbers [13], it is required to choose a complete set of wave functions  $\langle \mathbf{r} | \{Q\sigma\}, \{\mathbf{R}_i^c\} \rangle$  characterizing single-particle electronic states with the energy  $E(\{Q\})$

$$\psi_e^+(\mathbf{r}) = \sum_{\{Q\sigma\}} \langle \{Q\sigma\}, \{\mathbf{R}_i^c\} | \mathbf{r} \rangle a_{\{Q\sigma\}}^+, \quad \psi_e(\mathbf{r}) = \sum_{\{Q\sigma\}} \langle \mathbf{r} | \{Q\sigma\}, \{\mathbf{R}_i^c\} \rangle a_{\{Q\sigma\}}, \quad (5)$$

in the external field of nuclei. Here  $a_{\{Q\sigma\}}^+$  and  $a_{\{Q\sigma\}}$  are the creation and annihilation operators of electrons in the state  $\langle \mathbf{r} | \{Q\sigma\}, \{\mathbf{R}_i^c\} \rangle$ ,  $\{Q\sigma\}$  is the set of quantum numbers, including the spin number  $\sigma$  (hereafter, for simplicity, spin indices are not considered). In

the problem under consideration the set of coordinates  $\{\mathbf{R}_i^c\}$  of nuclei plays the role of eigenvalue parameters. In this case, single-particle electronic states in the external field of nuclei are classified into two groups [17]. One (A) is localized (subscript "loc") states characterized by exponential spatial decrease with distance from localization centers. Among them are the single-center bound states of electrons in atoms, two-center ones in molecules, etc. Another group (B) is delocalized (subscript "del") states in which the electron propagates throughout the system. The typical example of delocalized states are plane waves  $\langle \mathbf{r} | \mathbf{q} \rangle$ ,  $\langle \mathbf{r} | \mathbf{q} \rangle = 1/\sqrt{V} \exp(i\mathbf{q}\mathbf{r})$ ,  $\epsilon(q) = \frac{\hbar^2 q^2}{2m_e}$  which describe the behavior of the free electron with momentum  $\hbar\mathbf{q}$  and energy  $\epsilon(q)$ . Thus, in the optimum case, the complete set of wave functions for the representation (5) should describe both localized and delocalized states of electrons. However, there are many problems in this way. The first problem is "physical"; it is associated with the fact that localized electronic states vary as thermodynamic parameters of the CS are varied; this leads, in particular, to the Mott effect [18], i.e., disappearance of localized states. This means that the quantum-mechanical consideration is insufficient for determination of localized states; quantum statistics effects should also be considered. The second problem, to the solution of which this paper is devoted, is associated with the necessarily finite number of electronic states localized on one center. By the example of the hydrogen atom considered within quantum mechanics ignoring quantum statistics effects [13], it is known that the number of bound electronic state is infinite, which leads, in turn, to the divergence of not only the statistical sum for an individual atom, but also to the unlimited atomic size at any nonzero temperature [2]. Based on combinatory reasons, E. Fermi [7] has shown that the introduction of the finite size of atoms results in an exponential limitation of the statistical sum. It is easy to see that the statistical sum limitation to any maximum value of the principal quantum number  $n_{max}$  is also a simultaneous introduction of the finite size of the atom. The absence of limitation, i.e, the case  $n = \infty$ , is the case corresponding to an infinite-size atom, which is meaningless (the size of the  $n$ -th orbit of the hydrogen atom is  $R_n = n^2 a_0$ , where  $a_0$  is the Bohr radius) [19]. Hence, it is impossible to correctly use the "single-center" (in the sense of the localization center) approximation in the description of localized states. In this case, the transition to the "single-center" approximation is meaningful when the condition

$$\langle R_a \rangle \ll \langle r \rangle_c, \quad \langle r \rangle_c = \left( \frac{4\pi n_c}{3} \right)^{-1/3}, \quad (6)$$

is satisfied, where  $\langle R_a \rangle$  is the "atom" size and  $\langle r \rangle_c$  is the average distance between nuclei (see below).

The consideration of the quantum statistics effects (with the opportunity to pass to the thermodynamic limit) means that localized electronic states for a separated nucleus should be considered taking into account that the CS, as a system of many identical particles, contains many other electrons (electronic states). However, the multiplicity of noninteracting electrons is already formally taken into account in the used formalism of secondary quantization (1), (2), (5).

The divergence directly follows from the definition of the electron distribution function  $f_e(E(\{Q\}))$  in states  $\langle \mathbf{r} | \{Q\}, \{\mathbf{R}_i^c\} \rangle$  with energy  $E(\{Q\})$

$$f_e(E) = \langle a_{\{Q\}}^+ a_{\{Q\}} \rangle^{(GE)} = \left\{ \exp \left( \frac{E - \mu_e}{T} \right) + 1 \right\}^{-1}, \quad \langle N_e \rangle^{(GE)} = \sum_{\{Q\}} f_e(E), \quad (7)$$

when using energy levels of the hydrogen atom as energies. It remains to hope that the "effective" consideration of the electron-electron interaction while retaining the single-particle consideration will make it possible to solve the problem of the finite number of bound states in the "atom", i.e., in the "single-center" approximation for wave functions (it is clear that the "multicenter" problem for localized electronic states is in principle unsolvable),

$$\langle \mathbf{r} | \{loc\}, \{\mathbf{R}_i^c\} \rangle \rightarrow \langle \mathbf{r} - \mathbf{R}_i^c | n \rangle \equiv \varphi_n(\mathbf{r} - \mathbf{R}_i^c), \quad E(n, \{loc\}) \rightarrow E_n. \quad (8)$$

In this case, the "atom" size in the "single-center" approximation, taking into account (7) and (8), can be defined for quantum statistics as follows

$$\langle R_a \rangle^2 = \int r^2 \sum_n f_e(E_n) |\varphi_n(r)|^2 d\mathbf{r}. \quad (9)$$

We emphasize that such quasiparticles - "atoms" are not identical to atoms commonly used in quantum mechanics. The difference is caused by the fact that any of one of a very large (infinite in the thermodynamic limit) number of electrons can be found in the corresponding electronic state of the "atom" due to the identity, which is reflected in the statistical description of such a system. Thus, electronic states in "atoms" will depend on the thermodynamic parameters, i.e., the temperature  $T$  and average density of the number of electrons  $n_e^{(0)}$  (or on the chemical potential  $\mu_e$ ) [2].

We note that electronic states are considered in the random field of nuclei. In this case, the role of quantum numbers for both "localized" (with discrete energy spectrum) and "delocalized" (with continuous energy spectrum) electronic states is played by the energy itself of the corresponding state and the spin quantum number [20]. For "localized" states, this set of quantum numbers can be complemented by coordinates of localization centers (nuclei)  $\{\mathbf{R}_i^c\}$  [20], since electronic states with this energy can become localized at different points of the system. In this sense, we can speak of degeneracy with respect to the quantities  $\{\mathbf{R}_i^c\}$  which, therefore, can be considered as "quantum" numbers. In this case, the term "quantum number" should be understood in a certain conditional meaning: the vectors  $\{\mathbf{R}_i^c\}$  and their components are not eigenvalues of any operator having an effect on "electronic" variables.

### III. FINITE ATOM IN HARTREE-FOCK APPROXIMATION

Further, let us consider the system of electrons in the external field of nuclei within the self-consistent Hartree-Fock approximation for quantum statistics [15]. Then the complete set of wave functions  $\langle \mathbf{r} | \{Q\}, \{\mathbf{R}_i^c\} \rangle$  and the corresponding energy spectrum  $E(\{Q\})$  of the multicenter problem are determined from the set of equations

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m_e} + \int [u_{ec}(\mathbf{r} - \mathbf{r}_1) n_c(\mathbf{r}_1) + u_{ee}(\mathbf{r} - \mathbf{r}_1) \langle n_e(\mathbf{r}_1) \rangle] d\mathbf{r}_1 \right\} \langle \mathbf{r} | \{Q\} \rangle - \int u_{ee}(\mathbf{r} - \mathbf{r}_1) \langle n_e(\mathbf{r}, \mathbf{r}_1) \rangle \langle \mathbf{r}_1 | \{Q\} \rangle d\mathbf{r}_1 = E(\{Q\}) \langle \mathbf{r} | \{Q\} \rangle, \quad (10)$$

In (10), the term with function  $\langle n_e(\mathbf{r}) \rangle = \langle n_e(\mathbf{r}, \mathbf{r}_1) \rangle|_{\mathbf{r}=\mathbf{r}_1}$  corresponds to the Hartree approximation. The term with function  $\langle n_e(\mathbf{r}, \mathbf{r}_1) \rangle = \sum_{\{Q\}} \langle \mathbf{r} | \{Q\} \rangle \langle \{Q\} | \mathbf{r}_1 \rangle f_e(E(\{Q\}))$  in (10) corresponds to the Fock approximation. Nonlocal structure of the Fock term in (10) significantly complicates the problem. However, its consideration is conceptually necessary. First, in the Hartree approximation, the states  $\langle \mathbf{r} | \{Q\}, \{\mathbf{R}_i^c\} \rangle$  are not orthogonal to each other [13]. Second, the consideration of the Fock approximation allows elimination of the so-called "self-action". As it is easy to check from (10), the state  $\langle \mathbf{r} | \{Q\} \rangle$  in the Hartree-Fock approximation is determined only by other states, in contrast to the Hartree approximation [13]. The set of equations (10) includes not only localized, but also delocalized states, to describe which the "single-center" approximation is inapplicable. Taking into account that we are interested in justification of the finiteness of the number of localized states, let us

simplify the set of equations (10) under the assumption that the number of delocalized states is very small. This can be done using the properties of the Fermi-Dirac distribution (7) for the function  $f_e(E)$  in (10). Let us perform the further consideration without loss of generality immediately for the case of hydrogen,  $z_c = 1$ ,  $\langle N_e \rangle^{(GE)} = N_c$ . Let us suppose that for the energy  $E_0$  of the ground single-particle localized state, energies  $E_{exc}$  of each of other states, including delocalized states, and the chemical potential  $\mu_e$  of electrons, the following relations are valid

$$E_0 < 0, \quad |E_0| \gg T, \quad |E_0 - E_{exc}| \gg T, \quad E_0 < \mu_e < 0. \quad (11)$$

Then, according to (7),

$$f_e(E_0) \cong 1 - \exp\left(\frac{E_0 - \mu_e}{T}\right) \cong 1, \quad f_e(E_{exc}) \cong \exp\frac{\mu_e - E_{exc}}{T} \ll 1. \quad (12)$$

We further take into account that the number of single-particle localized states is proportional to the number of localization centers; in the "single-center" approximation, it is proportional to the number of nuclei  $N_c$ . We also assume that the delocalized states are close to corresponding plane waves. Then, with required accuracy, we can consider that the energy levels of delocalized states are defined by the energy  $\epsilon(q)$  of the free electron,  $E(\{del\}) \rightarrow \epsilon(q)$ . Thus, taking into account

$$\langle N_e \rangle^{(GE)} = \sum_{\{Q\}} f_e(E(\{Q\})) \rightarrow N_c \sum_n f_e(E_n) + \sum_q f_e(\epsilon(q)), \quad (13)$$

and (7)-(12), we find the equation for determining the chemical potential  $\mu_e$  of electrons in the "single-center" approximation for localized states,

$$\langle N_e \rangle^{(GE)} = N_c \left\{ 1 - \exp\left(\frac{E_0 - \mu_e}{T}\right) + \sum_{n \neq 0} \exp\left(\frac{\mu_e - E_n}{T}\right) \right\} + \sum_q \exp\left(\frac{\mu_e - \epsilon(q)}{T}\right). \quad (14)$$

Then, taking into account (11) and the equality

$$\sum_q \exp\left(\frac{\mu_e - \epsilon(q)}{T}\right) = V \int \exp\left(\frac{\mu_e - \epsilon(q)}{T}\right) \frac{d^3q}{(2\pi)^3} = \frac{V}{\Lambda^3} \exp\left(\frac{\mu_e}{T}\right), \quad \Lambda = \left(\frac{2\pi\hbar^2}{m_e T}\right)^{\frac{1}{2}} \quad (15)$$

from (14), we find

$$\mu_e = E_0 - \frac{T}{2} \ln \left\{ \sum_{n \neq 0} \exp\left(\frac{E_0 - E_n}{T}\right) + \frac{1}{n_e \Lambda^3} \exp\left(\frac{E_0}{T}\right) \right\}. \quad (16)$$

Thus, conditions (11) for the chemical potential are satisfied when

$$\sum_{n \neq 0} \exp\left(\frac{E_0 - E_n}{T}\right) + \frac{1}{n_e \Lambda^3} \exp\left(\frac{E_0}{T}\right) < 1. \quad (17)$$

Taking into account (11), inequality (17) is valid for a limited number of localized states. According to (11), (12), (14), the contribution of delocalized states in the self-consistent Hartree-Fock approximation (10) can be neglected in a very wide range of thermodynamic parameters satisfying the condition  $\sum_{n \neq 0} \exp\left(-\frac{E_n}{T}\right) \gg \frac{1}{n_e \Lambda^3}$ . When determining localized states and the corresponding energy spectrum, we can consider with required accuracy that the ground state is "populated",  $f_e(E_0) \cong 1$  and all excited states are "free",  $f_e(E_{exc}) \cong 0$ . Thus, when relations (11), (16), (17) are valid, the set of equations of the self-consistent Hartree-Fock approximation (10) can be written for localized states in the "single-center" approximation (8) (the nucleus with charge  $z_c = 1$  is at the coordinate origin),

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{e^2}{r} + \int u_{ee}(\mathbf{r} - \mathbf{r}_1) |\varphi_0(r)|^2 d\mathbf{r}_1 \right\} \varphi_n(r) - \int u_{ee}(\mathbf{r} - \mathbf{r}_1) \varphi_0(r) \varphi_0^*(r_1) \varphi_n(r_1) d\mathbf{r}_1 = E_n \varphi_n(r), \quad (18)$$

It immediately follows from (18) that the wave function  $\varphi_0(\mathbf{r})$  and the ground state energy  $E_0$  are identical to the similar quantities for the electron ground state in the hydrogen atom [13],  $\varphi_0(r) = (\pi a_0^3)^{-\frac{1}{2}} \exp\left(-\frac{r}{a_0}\right)$ ,  $E_0 = -\frac{m_e e^4}{\hbar^2}$ , where  $a_0$  is the Bohr radius. The "excited" localized states ( $n > 1$ ) are characterized by the energies  $E_n$  and differ from corresponding states in the hydrogen atom, which makes it possible, in particular, to remove the known "Coulomb degeneracy" of energy levels [13]. Taking into account the explicit form of the Fourier components of the Coulomb interaction potential (2), we can calculate the Hartree term, i.e., the last braced term in (18),

$$u_H(r) = \int u_{ee}(\mathbf{r} - \mathbf{r}_1) |\varphi_0(\mathbf{r})|^2 d\mathbf{r}_1 = \frac{e^2}{r} - \frac{e^2}{r} \left(1 + \frac{r}{a_0}\right) \exp\left(-\frac{2r}{a_0}\right). \quad (19)$$

Further analytical calculations seem impossible. As in quantum-mechanical calculations, in view of the nonlocality of the Fock term, equations (18), taking into account (19), are solved using iterations [13,14]. However, by analogy with the states in the hydrogen atom [13], we can assume that the limit relations

$$\lim_{r \rightarrow 0} \varphi_n(r) = c_n < \infty, \quad \varphi_n(r \rightarrow \infty) \sim \exp\left(-\frac{a_n r}{a_0}\right), \quad 0 < a_n < 1. \quad (20)$$



are valid for functions  $\varphi_n(r)(n > 1)$ .

In this case, the Fock term in (18) and (19) can be written in the "local" form

$$\int u_{ee}(\mathbf{r} - \mathbf{r}_1) \varphi_0(r) \varphi_0^*(r_1) \varphi_n(r_1) d\mathbf{r}_1 = u_F^n(r) \varphi_n(r), \quad (21)$$

$$u_F^n(r) = \varphi_0(r) \varphi_n^{-1}(r) \int u_{ee}(q) \exp(i\mathbf{q}\mathbf{r}) \phi_{0n}(q) \frac{d^3q}{(2\pi)^3}, \quad (22)$$

$$\phi_{0n}(q) = \int \varphi_0(r) \varphi_n(r) \exp(-i\mathbf{q}\mathbf{r}) d\mathbf{r}. \quad (23)$$

According to (20) and (23),

$$\lim_{q \rightarrow \infty} \phi_{0n}(q) = 0, \quad \lim_{q \rightarrow 0} \phi_{0n}(q) = \phi_{0n}(q=0) = \int \varphi_0(r) \varphi_n(r) d\mathbf{r} = 0. \quad (24)$$

due to the orthogonality of the functions  $\varphi_0(r)$  and  $\varphi_n(r)$ . Then it immediately follows from (21)-(24) that

$$\lim_{r \rightarrow 0} u_F^n(r) = u_n = \text{const}, \quad u_F^n(r \rightarrow \infty) \sim \exp\left(-\frac{\gamma_n r}{a_0}\right), \quad \gamma_n > 0. \quad (25)$$

Hence, we come to the conclusion that the function  $\varphi_n(r)$  is defined as the wave function satisfying the Schrodinger equation,

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + U_n(r)\right) \varphi_n(r) = E_n \varphi_n(r),$$

$$U_n(r \rightarrow 0) = -\frac{e^2}{r}, \quad U_n(r \rightarrow \infty) \sim \exp\left(-\frac{\gamma_n r}{a_0}\right). \quad (26)$$

Thus, the initial assumptions (20) are valid. Furthermore, the asymptotic behavior of the potential  $U_n(r)$  is similar to the behavior of the known Yukawa potential [21]. As is known, at certain parameters of the Yukawa potential, it will not contain the bound (localized) state [22]. As applied to the problem under consideration, this means that the number of localized states in the hydrogen "atom" is limited.

Using the results obtained above, it is easy to see that the free energy  $F^{CS}$  (3) of the Coulomb system under consideration equals

$$F^{CS} = -N_c T \left\{ 1 + \ln \left[ \left( \frac{m_c T}{2\pi \hbar^2} \right)^{3/2} \frac{f_e(T)}{n_c} \right] \right\}, \quad f_e(T) = \exp\left(-\frac{E_0}{T}\right) \quad (27)$$

if the conditions (6), (11), (16), (17) are valid.

The relation (27) corresponds the free energy of the ideal gas of new quasiparticles - "atoms", in which electron is in the ground state (see, e.g., [16]).

Summarizing the above consideration, it can be assert that the statistical sum and the hydrogen "atom" size are finite when using the self-consistent quantum-statistical Hartree-Fock approximation. In this case, in the above approximation (11) for the chemical potential of electrons, the "atom" size (9) is independent of the density of the number of particles and of temperature in the system and is defined only by the Bohr radius in a wide range of thermodynamic parameters. For low temperature the developed approach provides the rigorous derivation of the atomic free energy (27), written earlier on the basis of physical reasons. On the basis of the above derivation, it is evident that the finiteness of the number of localized states leads to the finite free energy of the CS at arbitrary temperature.

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